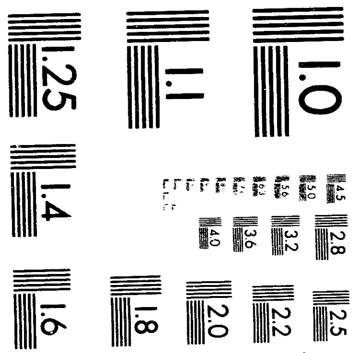
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RTI

RESEARCH TRIANGLE INSTITUTE

DOE Contract No. DE-AC21-93MC30010
RTI Project No. 96U-5666
July 1, 1993 to September 30, 1993

BENCH-SCALE DEMONSTRATION OF HOT-GAS DESULFURIZATION TECHNOLOGY

Quarterly Technical Progress Report

Submitted to

U.S. Department of Energy
Morgantown Energy Technology Center
3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

POST OFFICE BOX 12194 RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709-2194

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Submitted by

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1.0 INTRODUCTION AND SUMMARY

The U.S. Department of Energy (DOE), Morgantown Energy Technology Center (METC), is sponsoring research in advanced methods for controlling contaminants in hot coal gasifier gas (coal gas) streams of integrated gasification combined-cycle (IGCC) power systems. The programs focus on hot-gas particulate removal and desulfurization technologies that match or nearly match the temperatures and pressures of the gasifier, cleanup system, and power generator. The purpose is to eliminate the need for expensive heat recovery equipment, reduce efficiency losses due to quenching, and minimize wastewater treatment costs.

Hot-gas desulfurization research has focused on regenerable mixed-metal oxide sorbents which can reduce the sulfur in coal gas to less than 20 ppmv and can be regenerated in a cyclic manner with air for multicycle operation. Zinc titanate (Zn_2TiO_4 or $ZnTiO_3$), formed by a solid-state reaction of zinc oxide (ZnO) and titanium dioxide (TiO_2), is currently the leading sorbent. Overall chemical reactions with Zn_2TiO_4 during the desulfurization (sulfidation)-regeneration cycle are shown below:

Sulfidation: $Zn_2TiO_4 + 2H_2S \rightarrow 2ZnS + TiO_2 + 2H_2O$

Regeneration: $2ZnS + TiO_2 + 3O_2 \rightarrow Zn_2TiO_4 + 2SO_2$

The sulfidation/regeneration cycle can be carried out in fixed-bed, moving-bed, or fluidized-bed reactor configuration, and all three types of reactors are slated for demonstration in the DOE Clean Coal Technology program. The fluidized-bed reactor configuration is most attractive because of several potential advantages including faster kinetics and the ability to handle the highly exothermic regeneration to produce a regeneration offgas containing a constant concentration of SO_2. However, a durable attrition-resistant sorbent in the 100- to 400-μm size range is needed for successful fluidized-bed operation.

The SO_2 in the regeneration offgas needs to be disposed of in an environmentally acceptable manner. Options for disposal include recycle to the gasifier in which an in-bed desulfurization sorbent such as dolomite or limestone is being employed, conversion to sulfuric acid, and conversion to elemental sulfur. All three options are being pursued and/or proposed in the Clean Coal Technology program. Elemental sulfur recovery is the most attractive option because sulfur can be easily transported, stored, or disposed. However, elemental sulfur recovery using conventional methods from an offgas containing low levels of SO_2 (typically 3%) is an expensive proposition. An efficient, cost-effective method is needed to convert the SO_2 in the regenerator offgas directly to elemental sulfur.

Research Triangle Institute (RTI) with DOE/METC sponsorship has been developing zinc titanate sorbent technology since 1986. In addition, RTI has been developing the Direct Sulfur Recovery Process (DSRP) with DOE/METC sponsorship since 1988. Fluidized-bed zinc titanate desulfurization coupled to the DSRP is currently the most advanced and attractive technology for sulfur removal/recovery for IGCC systems, and it has recently been proposed in a Clean Coal Technology project.

RTI has developed a durable fluidized-bed zinc titanate sorbent, ZT-4, which has shown excellent durability and reactivity over 100 cycles of testing at 750 to 780°C. In bench-scale development tests, it consistently reduced the H_2S in simulated coal gas to <20 ppmv and demonstrated attrition resistance comparable to fluid cracking catalysts. The sorbent is manufactured by a commercially scalable granulation technique using commercial equipment available in sizes up to 1,000 L. The raw materials used are relatively inexpensive, averaging about $1.00/lb. It is anticipated that the impact on cost of electricity (COE) due to sorbent replacement for attrition will be less than 0.5 mil/kWh. ZT-4 has recently been tested independently by the Institute of Gas Technology (IGT) for Enviropower/Tampella Power, and showed no reduction in reactivity and capacity after 10 cycles of testing at 650°C.

In the DSRP SO_2 is catalytically reduced to elemental sulfur using a small slip stream of the coal gas at the pressure and temperature conditions of the regenerator offgas. A near-stoichiometric mixture of offgas and raw coal gas (2 to 1 mol ratio of reducing gas to SO_2) reacts in the presence of a selective catalyst to produce elemental sulfur directly:

$$2H_2 + SO_2 \rightarrow (1/n)Sn + 2H_2O$$

$$2CO + SO_2 \rightarrow (1/n)Sn + 2CO_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

The above reactions occur in Stage I of the process, and convert up to 96% of the inlet sulfurous gases (H_2S+SO_2) to elemental sulfur, which is recovered by cooling the outlet gas to condense out the sulfur. Adjusting the stoichiometric ratio of coal gas to regenerator offgas to 2 at the inlet of the first reactor also controls the Stage I effluent stoichiometry since any H_2S and COS produced (by the reactions: $3H_2 + SO_2 \rightarrow H_2S + 2H_2O$, and $3CO + SO_2 \rightarrow COS + 2CO_2$) yields an H_2S + COS to SO_2 ratio of 2 to 1. The effluent stoichiometry plays an important role in the Stage II DSRP reactor (operated at 275 to 300°C), where 80% to 90% of the remaining sulfur species is converted to elemental sulfur via $COS + H_2O \rightarrow H_2S + CO_2$ and $2H_2S + SO_2 \rightarrow (3/n)Sn + 2H_2O$. The overall sulfur recovery is projected at 99.5%.

The DSRP technology is also currently at the bench-scale development stage with a skid-mounted system ready for field testing. Very recently, the process has been extended to fluidized-bed operation in the Stage I reactor. Fluidized-bed operation has proved to be very successful with conversions up to 94% at space velocities ranging from 8,000 to 15,000 scc/cc·h. Overall conversion in the two stages following interstage sulfur and water removal has ranged up to 99%.

A preliminary economic study in which the two-stage DSRP was compared to conventional processes indicated the economic attractiveness of the DSRP. For 1% to 3% sulfur coals the installation costs ranged from 25 to 40 $/kW and the operating costs ranged from 1.5 to 2.7 mil/kWh.

Through bench-scale development, both fluidized-bed zinc titanate and Direct Sulfur Recovery Process (DSRP) technologies have been shown to be technically and economically attractive. The demonstrations to date, however, have only been conducted using simulated (rather than real) coal gas and simulated regeneration off-gas. Thus, the effect of trace contaminants in real coal gases on the sorbent and DSRP catalyst is currently unknown. Furthermore, the zinc titanate work to date has emphasized sorbent durability development rather than database development to permit design of large-scale reactors. Discussions with fluidized-bed experts have indicated that data from a larger reactor than the present are required for scaleup, especially if the material does not have particle sizes similar to fluid catalytic cracking catalysts (typically ~80 μm). The fluidized-bed zinc titanate technology uses 100- to 400-μm particles. Finally, the zinc titanate desulfurization unit and DSRP have not been demonstrated in an integrated manner.

1.1 PROJECT OBJECTIVES

The goal of this project is to continue further development of the zinc titanate desulfurization and DSRP technologies by

- Scaling up the zinc titanate reactor system;
- Developing an integrated skid-mounted zinc titanate desulfurization - DSRP reactor system;
- Testing the integrated system over an extended period with real coal-gas from an operating gasifier to quantify the degradative effect, if any, of the trace contaminants present in coal gas;
- Developing an engineering database suitable for system scaleup; and
- Designing, fabricating and commissioning a larger DSRP reactor system capable of operating on a six-fold greater volume of gas than the DSRP reactors used in the bench-scale field tests.

1.2 MILESTONE ACCOMPLISHMENTS FOR CURRENT QUARTER

Due to the delays encountered with the Construction Permit Application, the Project Task Schedule and Milestones was revised and is attached to this report as Appendix A. During the current reporting period, the Kick-off Meeting and the Project Planning Meeting were held with DOE/METC. Tasks 1 and 2 progressed with the submission to DOE/METC of the revised Construction Permit Application Package, and with preliminary discussions of the trailer design and layout with the manufacturer.

2.0 TECHNICAL DISCUSSION:

2.1 KICK-OFF MEETING AND PROJECT PLANNING MEETING

The Kick-off and Project Planning Meetings were held with DOE/METC on July 1 and August 5, 1993, respectively. The background and motivation for the project were reviewed, along with METC's requirements for RTI and the specific tasks to be performed. RTI also presented a preliminary schedule for completion of the tasks. During the Project Planning Meeting, RTI submitted a list of requirements (gas, water and electricity supplies, sewer access, and disposal) needed at the METC gasifier site for the experiment. Furthermore, METC informed RTI that a Construction Permit Application is needed to satisfy the Safety Analysis and Review System (SARS) Procedure.

2.2 CONSTRUCTION PERMIT APPLICATION PACKAGE

The bulk of this reporting period was occupied by the Construction Permit Application. A first draft was submitted to DOE/METC's Process Safety Committee (PSC) for informal review on September 2, 1993. The PSC's suggestions and concerns were addressed and incorporated into a revised Construction Permit Application, which was submitted to DOE/METC on October 18, 1993.

2.3 TRAILER DESIGN AND LAYOUT

The trailer layout, as currently envisioned, is attached as Appendix I. Preliminary discussions with RTI's Safety and Occupational Health Office and the Heating, Ventilation and Air Conditioning (HVAC) section were conducted. The safety considerations for the trailer were submitted for review in the Construction Permit Application. The HVAC system suggested for the trailer is a dual-unit, 12-ton HVAC system to provide ventilation and cooling to counteract the heat produced by the equipment. A dual-unit system is necessary for operating conditions in which little or no HVAC load is needed when outdoor temperatures are very low. The primary unit will have 4 tons of refrigeration capacity with hot-gas bypass on the refrigeration system to provide 50% unloading and will introduce 320 scfm of outdoor air distributed throughout the trailer. This will change the air within the trailer four times per hour, including 90 scfm used to vent the instruments (50 scfm), the liquid-SO_2 room (20 scfm), and the zinc titanate desulfurization/DSRP system (20 scfm). This 90 scfm will be piped to the METC incinerator. The remaining 230 scfm of outdoor air will be vented to the atmosphere through two exhaust fans located at opposite ends of the trailer and wired to operate whenever the HVAC system is in operation.

The secondary unit will have 8 tons of refrigeration capacity and 50% capacity reduction via split refrigeration circuitry and an appropriate air distribution system. Both HVAC units will be controlled in steps by multistage thermostats.

RTI has discussed and is still discussing these requirements with the trailer manufacturer, and will request that this system be provided on the delivered trailer.

2.4 REVISED PROJECT SCHEDULE AND MILESTONES

Due to the delays caused by the preparation of the Construction Permit Application Package, the Project Schedule and Milestones was revised to that shown in Appendix A. The main delay is to Task 2, Reactor System Fabrication, Delivery and Installation, pending the outcome of the DOE/METC review of RTI's Construction Permit Application.

3.0 PLANS FOR NEXT QUARTER

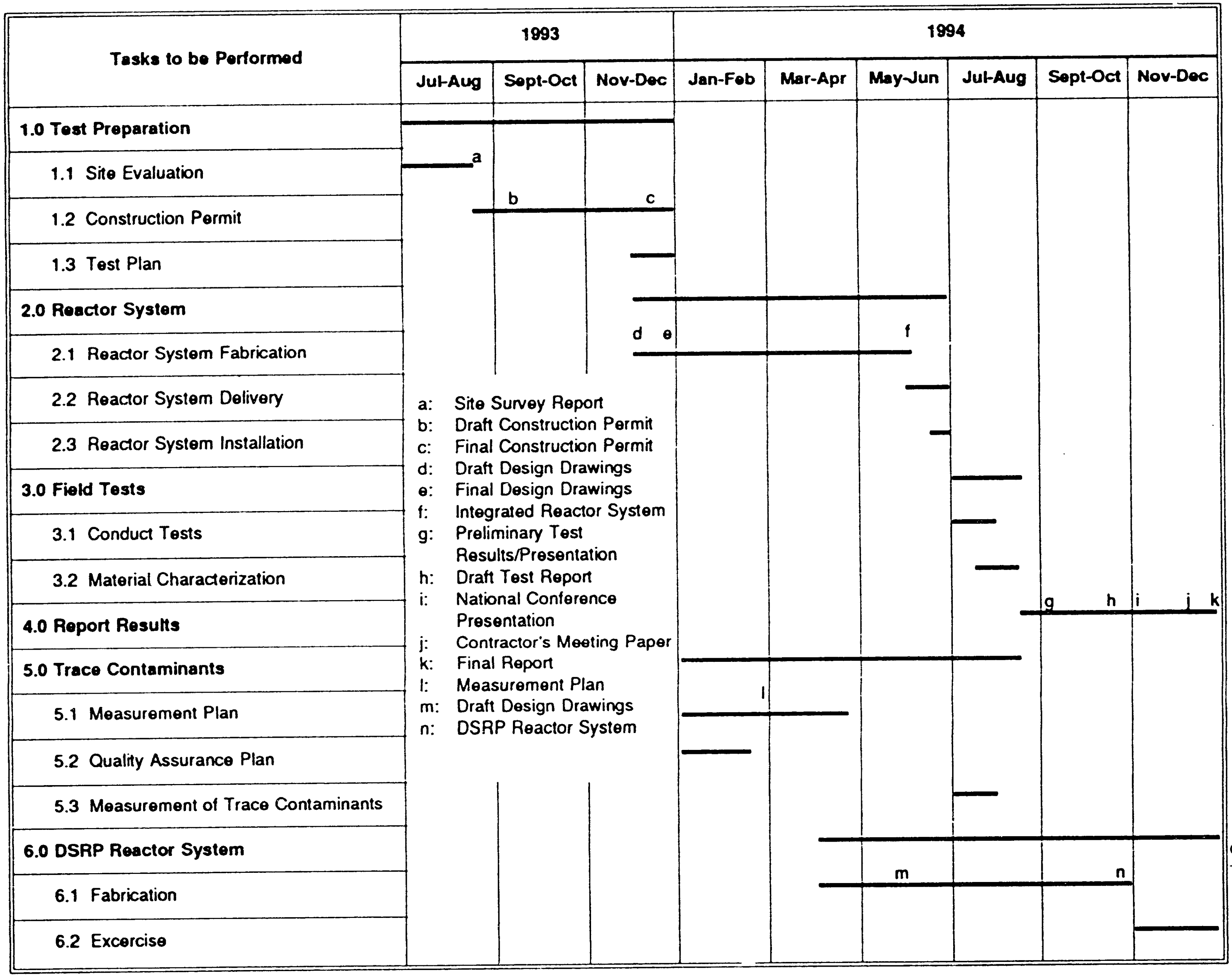
For the next reporting period we will progress through Tasks 1 and 2 by:

1. Reviewing the submitted Construction Permit Application Package with DOE/METC and making any necessary additions and/or changes;
2. Developing an Operation and Test Plan detailing the sequence and number of tests to be conducted at the test sight;
3. Receiving from Allison Gas Turbines the major components of the zinc titanate desulfurization unit;
4. Continuing discussions on trailer design and requirements with the manufacturer;
5. Finalizing the safety interlock and process control systems for the experiment;
6. Issuing Final Design Drawings for the integrated zinc titanate desulfurization/DSRP system; and
7. Ordering safety equipment and process control components.

Appendix A

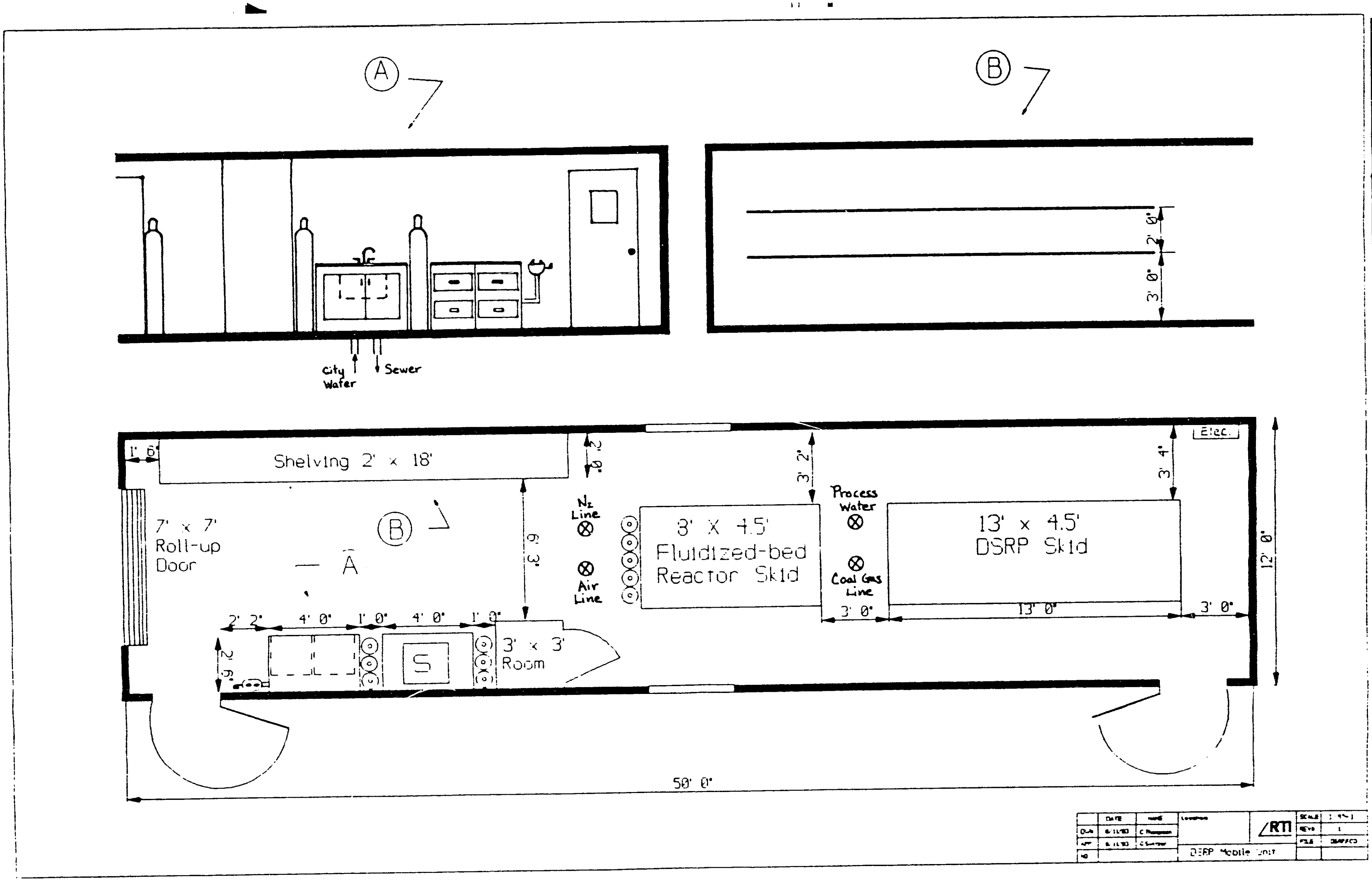
Revised Project Schedule

Project Schedule and Milestones



Appendix B

Layout of the Trailer (Mobile Laboratory)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1' 6"
Shelving 2' x 18'
2' 0"
3' 2"
3' 4"
Elec.
Process Water
7' x 7' Roll-up Door
B
A
6' 3"
N2 Line
Air Line
3' X 4.5' Fluidized-bed Reactor Skid
13' x 4.5' DSRP Skid
Coal Gas Line
12' 0"
3' 0"
13' 0"
3' 0"
2' 2"
4' 0"
1' 0"
4' 0"
1' 0"
2' 6"
S
3' x 3' Room
50' 0"
DATE
NAME
RTI
SCALE
REV
DSRP Mobile Unit

DATE FILMED

3 / 7 / 94

END